Impact of Ligand Substitution Patterns in Models for Mononuclear Molybdenum Containing Enzymes

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Except for nitrogenases, molybdenum-containing enzymes catalyze a wide range of oxygen atom transfer reactions of great importance for ubiquitous metabolic pathways. In their active sites the metal center is coordinated generally by one or two pyranpterindithiolate entities and at least one terminal oxo or sulfur ligand. With respect to their structural properties, Hille has classified these molybdenum enzymes into three families.[1]

In recent years scores of excellent structural and functional analogues relevant to molybdenum oxotransferases were described by Enemark, Holm and others.[2] In our group a variety of new biomimetic model complexes were synthesized and completely characterized by X-ray crystallography as well as spectroscopic methods. For the preparation of the mononuclear species we focused on bulky tridentate and potentially heptadentate ligands comprising of ONS- or ON_2S_2-donorsets, respectively, based upon a comparable system.[3] They exhibit electron-withdrawing and -donating groups in *para*-position to a coordinating phenolic oxygen atom.

The influence of ligand substitution on spectroscopic properties of the model complexes as well as on their reactivity towards oxygen atom transfer reactions was examined. Depending on the electronic features of the substituent, a systematic shift of the IR bands assignable to ν(Mo=O) vibration was found. Kinetic investigations were performed by monitoring the reaction of selected complexes with model substrates by UV/vis- and ^{31}P-NMR-spectroscopy. They reveal a remarkable increase of the reaction rate by electron withdrawing groups.

The observed effects indicate the relevance of ligand control by variation of the substitution pattern and show a linear correlation with the Hammett σ values for the respective substituent.

[1] R. Hille, *Chem. Rev.* **1996**, *96*, 2757.
[2] e.g. J. H. Enemark, J. J. Cooney, J.-J. Wang, R. H. Holm, *Chem. Rev.* **2004**, *107*, 1175.
[3] L. Stelzig, S. Kötte, B. Krebs, *J. Chem. Soc., Dalton Trans.* **1998**, 2921.